Libby Superfund Site Operable Unit 3 Standard Operating Procedure

Date: February 7, 2008

SOP DUFF-LIBBY-OU3 (Rev. 0)

Title: SAMPLING AND ANALYSIS OF DUFF FOR ASBESTOS

APPROVALS:

TEAM MEMBER	SIGNATURE/TITLE	DATE
EPA Remedial Project Manager	Mary Goldade for Bonnie Project Chemist Bonita Lavelle, USEPA RPM	2/7/08
SOP Author	W J Brattin William Brattin, SRC	2/7/08

Revision No.	Date	Reason for Revision
0	02/07/2008	--

1.0 PURPOSE

The purpose of this Standard Operating Procedure (SOP) is to provide a standardized method for collection and analysis of duff samples for Libby amphibole asbestos (LA). Duff consists of the un-decomposed twigs, needles and other vegetation and the layer of partially- to fully-decomposed litter that occurs on top of the mineral soil in forested areas. This procedure will be used by USEPA Region 8 for the Remedial Investigation work for Operable Unit 3 performed at the Libby Asbestos Superfund site.

2.0 RESPONSIBILITIES

The Field Sampling Team Leader is responsible for ensuring that all duff samples are collected in accord with this SOP. The Laboratory Director is responsible for ensuring that duff samples provided to the laboratory for evaluation by this SOP are prepared and analyzed in accord with the requirements of this SOP. It is the responsibility of the Field Sampling Team Leader and the Laboratory Director to communicate the need for any deviations from the SOP with the appropriate USEPA Region 8 Remedial Project Manager or Regional Chemist.

3. 0 EQUIPMENT

3.1 *Field Equipment*

- Ziploc® plastic bags
- sample identification labels
- GPS unit
- field log book
- field sample data sheet(s)
- ink pen
- clear packaging tape

3.2 Laboratory Equipment /Reagents

- Large aluminum trays
- Drying oven
- Large metal tray(s) (large enough for duff sample to cover bottom up to 1/2 in.)
- Muffle furnace
- Glass stirring rods
- Fume hood
- HEPA filtered hood
- Reagent grade or better acetone
- Reagent grade or better HCl
- Fiber-free deionized water (FDI water)
- Ultrasonic bath, producing a rate of energy deposition in the range of 0.08-0.12 MW/m^3
- Disposable plastic filter funnel apparatus

- Disposable filter funnels with straight sides [VWR # 145-0020]
- Culture dishes [VWR # 25388-581, case of 500]
- 47 mm 0.45 micron MCE or 0.4 micron PC filters
- Kim wipes or alternative paper
- Ziploc plastic bags
- Glass petri dishes
- Glass microscope slides
- Low temperature plasma asher
- Vacuum evaporator (carbon coater)
- Graphite or carbon rods
- HEPA laminar flow hood
- Acetone vapor generator
- Grids
- Fine forceps
- Grid storage boxes
- Jaffe wick or sponge
- Transmission electron microscope with the following capabilities:
  - 100 Kev
  - fine probe size <250 nm
  - Energy Dispersive X-Ray Analysis (EDXA)
  - Selective Area Electron Diffraction (SAED)

4.0 METHOD SUMMARY

A duff sample is collected by hand at a selected field location and placed in a plastic bag. Duff samples are prepared for analysis by high temperature ashing to remove organic matter. The residue is then analyzed for LA by transmission electron microscopy (TEM) and/or by Polarized Light Microscopy (PLM), as specified in the project-specific Sampling and Analysis Plan (SAP).

5.0 SAMPLE COLLECTION

Duff samples should be collected from the soil sampling stations specified in the project-specific SAP. At each specified sampling station, collect any fresh or partially decayed organic debris (e.g., twigs, leaves, pine needles) using a freshly-gloved hand from the soil surface within an area that is approximately 6 in. x 6 in. Care should be taken to ensure that the top layer of soil beneath the organic debris is not included in the duff material sample. Place the duff material into a large, air-tight, re-sealable plastic bag. Label the bag with the same sample identifier as the soil field sample, and place clear packaging tape over the sample identifier label.

Attachment A provides a Field Sample Data Sheet (FSDS) for recording field information on each duff sample. [Note: in some cases, an alternative FSDS may be specified and provided in the project specific SAP]. Note any special circumstances or conditions about the sampling location. Obtain and record the GPS coordinates of the sampling location on the FSDS form.

6.0 SAMPLE PREPARATION AND ANALYSIS

6.1 Drying and Ashing

Weigh and record the tare weight of a clean, dry aluminum tray of approximately quart size. Fill the aluminum tray to approximately ¾ full. The samples may be split across as many trays as may be needed, providing the samples' identification number is clearly marked on each tray. In addition, for tracking purposes each tray should possess a mark to make it unique and identifiable from the other trays. This identifier shall be recorded in the laboratory preparation logs. Each tray will need to be initially tared and then gravimetrically tracked through the process. Place the tray(s) with the sample into a drying oven. Heat to 60°C and hold at this temperature until weight stabilizes (at least 10 hours). Record the dry weight and calculate the mass of the dried duff sample by the difference.

Once samples are dried, they then shall be ashed. Weigh and record the tare weight of one or more clean metal pans capable of withstanding the heat of à 450°C oven. Working under a hood, transfer the dried duff to the tared pan(s), place a lid on the pan and move to a muffle furnace. Ramp up the furnace from a cold start to 450°C and hold at this temperature for 18 hours or until all organic matter is removed.

Allow the pan(s) to cool. Remove the lid(s), weigh and record the mass of the pan(s) plus the ashed residue. Calculate the mass of the ashed residue in each pan by difference. If the sample was ashed in more than one pan, compute the total mass of the ashed residue for the sample by summation across pans.

Under a laminar flow hood, slowly pour the ash from each sample into a Ziploc bag. If the sample was ashed in more than one pan, all the pans for that sample are combined into a single Ziploc bag. If the ash still retains some structure, seal the bag tightly and manipulate the ash by hand to reduce it to a fine homogenous powder. Invert the bag 3-4 times to thoroughly mix the ash.

All information regarding sample preparation shall be recorded using the sample preparation log sheet, presented as Attachment B.

6.2 TEM Analysis

Acid Treatment

Remove an aliquot of approximately 0.25 g of the well-mixed ash and place into a crucible. Record the weight (measured to an accuracy of ± 0.01 g) on the sample preparation data sheet (see Attachment B). To the ashed residue in the crucible, add just enough FDI water (approx 1-2 mL) to cover the surface of the residue. Slowly add concentrated HCl to the wetted ash (approx. 10-20 mL). Typically a visible effervescing is observed. Add the HCl slowly to keep this reaction controlled. A small glass stirring rod is useful at this point to gently stir the ash and expose all material to the acid.

If after 3-5 minutes there is no further visible reaction, proceed to the next step. If bubbling is still occurring, continue observation and gentle stirring for up to an additional 5 minutes.

Dilute the sample by adding FDI water directly to the crucible (approx 20 mL) using a squirt bottle. Pour the sample into an unused disposable 100 mL specimen container with lid. Rinse out any remaining residue from the crucible into the specimen container. Do not exceed 100 mL total volume. Bring the total volume to 100 mL with DI water.

Cap the specimen cup and agitate the sample by inversion 5 or 6 times. Loosen the cap slightly and sonicate for 2 minutes. After sonication, tighten the cap and then dry the exterior of the specimen container with a laboratory wipe.

Filtration

Agitate the sample by inversion 5 or 6 times. Withdraw an initial aliquot of 0.1 to 1 mL of sonicated sample. Transfer this aliquot into a new disposable specimen container with lid. Bring the volume up to approximately 100 mL with FDI water. Cap and agitate by inversion (5 or 6 times).

Filter this entire volume onto a 47 mm mixed cellulose ester (MCE) filter with 0.4 um pore size.

If the filter appears overloaded (overall particulate level > 20%), repeat the process above, selecting a smaller aliquot volume, as suggested by the degree of overloading. Conversely, if the filter looks too lightly loaded, filter a larger aliquot.

After filtration, transfer the filter membranes to individual disposable labeled Petri dishes with lids. With Petri dish covers ajar, gently air dry the filters in a HEPA protected environment.

TEM Examination

Prepare 3 grids for TEM analysis as detailed in International Organization for Standardization (ISO) TEM method 10312, also known as ISO 10312:1995(E). Utilize 2 grids for analysis, holding the third in case of problems. After analysis, archive all three grids for potential future reanalysis.

Counting rules

Examine the grids using TEM in accord with ISO 10312 and all relevant Libby site-specific modifications, including the most recent version of LB-000016, LB-000019, LB-000028, LB-000029, LB-000029a, LB-000030, LB-000053, and LB-000066. All fibrous amphibole structures that have appropriate Selective Area Electron Diffraction (SAED) patterns and Energy Dispersive X-Ray Analysis (EDXA) spectra, and having length greater than or equal to 0.5 um and an aspect ratio (length: width) $\geq$ 3:1, will be recorded on the Libby site-specific laboratory bench sheets and electronic data deliverable (EDD) spreadsheet for TEM analysis of duff samples. Data recording for chrysotile (if observed) is not required.

Stopping rules

The target analytical sensitivity for sample analysis should be specified in the SAP. In the absence of a project-specific target sensitivity, the default sensitivity should be 1E+07 $(grams)^{-1}$, which is likely to correspond to a mass fraction of less than about 0.005 grams asbestos per gram duff (dry wt). The analytical sensitivity is calculated using the following equation:

$$S = \frac{EFA}{GO \cdot Ago \cdot Mass \cdot F}$$

where:

S	=	Sensitivity (1/g dry wt)
EFA	=	Effective filter area (mm^2)
GO	=	Number of grid openings counted
Ago	=	Area of one grid opening (mm^2)
Mass	=	Mass of the dried (but not ashed) duff sample (g)
F	=	Fraction of the starting duff sample applied to the filter

Count the sample until one of the following occurs:

- The target sensitivity is achieved.
- A total of 50 or more LA structures are observed. In this case, counting may cease after completion of the grid opening that contains the 50^{th} LA structure.
- A total of 100 grid openings are counted without reaching the target sensitivity or observing 50 LA structures. In this event, the analysis should stop after completion of the 100^{th} grid opening.

TEM Data Deliverable

All data on the number, type and size of LA fibers observed during TEM analysis in the laboratory will be provided as an electronic data deliverable (EDD) using the most recent version of the spreadsheet developed for this purpose ("TEM Duff.xls"). The results for each sample will be expressed in terms of LA fibers per gram duff (dry weight), and also in terms of grams of LA per gram of duff (dry weight).

6.3 PLM Analysis

If analysis by PLM is called for in the project-specific SAP, the analysis will be performed on an aliquot of the ashed and homogenized residue using method PLM-VE as detailed in the most recent version of SOP SRC-LIBBY-03. PLM-VE is a semi-quantitative analytical method for asbestos that utilizes Libby-specific reference materials to allow assignment of samples into one of four "bins", as follows:

- Bin A (ND): non-detect
- Bin B1 (Trace): LA detected at levels lower than the 0.2% reference material
- Bin B2 (<1%): LA detected at levels lower than the 1% reference material but higher than the 0.2% reference material
- Bin C: LA detected at levels greater than or equal to 1%

A potential limitation to this approach is that the site-specific reference materials are based on LA in soil, not LA in ashed residue. This may introduce additional uncertainty into the results, but no reference materials based on ashed residue are presently available.

PLM-VE results will be recorded using the most recent version of the Libby site-specific EDD spreadsheet for PLM-VE analysis ("PLM (VE & PC) Data Sheet and EDD.xls").

7.0 QUALITY ASSURANCE

7.1 Field-Based Quality Assurance

Field Duplicates

Field duplicate duff samples will be collected at a frequency specified in the project-specific SAP. In the absence of such specification, the rate should be no less than 5%. Each field duplicate should be collected from a location close to the primary sample, and from an area of approximately equal size. Field duplicate samples should be labeled with a unique identifier. Sample details should be recorded on the appropriate soil FSDS, including the unique identifier of the "parent" field sample. Field duplicates are used to evaluate the sampling and analysis variability across duff samples. Unless indicated differently in the project-specific SAP, samples will not be qualified purely as a result of the difference between measured values between original and duplicate pairs.

7.2 Laboratory-Based Quality Assurance for TEM Analyses

Drying Blanks

For the purposes of this analysis, a drying blank will consist of one clean aluminum pan placed empty into the drying oven along with pans containing field samples of duff. After drying the duff samples, the clean tray will be removed and the surface will be rinsed with about 100 mL of FDI water into a clean container, which in turn will be filtered and prepared for TEM analysis. Detection of fibers on the drying blank filter will be taken as an indication of potential cross-contamination during drying.

Drying blanks should be prepared at a rate specified in the project-specific SAP. In the absence of a project-specific specification, drying blanks should be prepared at a rate of one per day that drying of samples is occurring. Unless indicated differently in the project-specific SAP, if the drying blank reports LA fibers, all samples in that drying batch will be assigned a qualifier to indicate the potential for cross-contamination.

Laboratory Blanks

A laboratory blank is a filter that is prepared by processing a clean crucible in the same way that a duff sample is prepared. That is, a clean crucible is treated by addition of FDI water and HCl, as described above. The contents of the crucible are then rinsed out, diluted to 100 mL, and an aliquot at least as large as the highest volume aliquot for the sample set is removed and used to prepare a filter for TEM examination. This type of blank is intended to indicate if contamination is occurring at any stage of the sample preparation procedure.

Laboratory blanks should be prepared at a rate specified in the project-specific SAP. In the absence of a project-specific specification, laboratory blanks should be prepared at a rate of 3%. Unless indicated differently in the project-specific SAP, if the laboratory blank reports LA fibers, all samples in that analytical batch will require re-preparation.

Filtration Blanks

A filtration blank is a clean filter that is prepared by passing 100 mL of laboratory FDI water through it. The purpose of this type of blank is to ensure that the filters are not contaminated in the laboratory, and that fluids used for diluting and processing samples are fiber-free.

Filtration blanks should be prepared at a rate specified in the project-specific SAP. In the absence of a project-specific specification, filtration blanks should be prepared at a rate of 2%. Unless indicated differently in the project-specific SAP, if the laboratory blank reports LA fibers, all samples in that analytical batch will require re-preparation.

Laboratory Duplicates

Laboratory duplicates will be prepared by applying a second aliquot of ashed residue suspension to a new filter, which is then prepared and analyzed in the same fashion as the original filter. The frequency of laboratory duplicates should be specified in the project-specific SAP. In the absence of such specification, the rate should be no less than 5%. Unless indicated differently in the project-specific SAP, samples will not be qualified purely as a result of the difference between measured values between original and duplicate pairs.

Recounts

The precision of TEM sample results should be evaluated by recounting selected grid openings in accord with the requirements specified in the most recent version of LB-000029.

7.3 Laboratory-Based Quality Assurance for PLM-VE Analyses

Laboratory Duplicates

Laboratory duplicate PLM-VE analyses will be prepared by examining a second aliquot of ashed and homogenized residue. The frequency of laboratory duplicates should be specified in the project-specific SAP. In the absence of such specification, the rate should be no less than 5%.

Unless indicated differently in the project-specific SAP, samples will not be qualified purely as a result of the difference between measured values between original and duplicate pairs.

8.0 REFERENCES

International Organization for Standardization. 1995. Ambient Air – Determination of asbestos fibres – Direct-transfer transmission electron microscopy method. ISO 10312:1995(E).

Phipps, R.L. 1985. Collecting, Preparing, Cross-dating and Measuring Tree Increment Cores. U.S. Geological Survey Water Resources Investigations Report 85-4148

Ward TJ, T Spear, J Hart, C Noonan, A Holman, M Getman, and JS Webber. 2006. Trees as Reservoirs for Amphibole Fibers in Libby, Montana. Science of the Total Environment 367: 460-465.

ATTACHMENT A

FIELD SAMPLING DATA SHEET (FSDS)

Sheet No.: Duff- _____

LIBBY FIELD SAMPLE DATA SHEET (FSDS) rev0
DUFF

Field Logbook No: _____ Page No: _____
Station ID: _____ Sampling Date: _____
GPS Coordinate System: _____ Elevation Coordinate System: _____
X coordinate: _____ Y coordinate: _____ Elevation: _____
Sampling Team: _____ Sampler Initials: _____
Station Comments: _____

Data Item	Sample 1	Sample 2	Sample 3
Index ID (place pre-printed label in field provided)			
Sample Time (hh:mm)			
Sample Type (circle one):	Grab Composite # of Composites: _____	Grab Composite # of Composites: _____	Grab Composite # of Composites: _____
Field QC Type (circle one):	FS (field sample) FD (field duplicate) For FD, Parent ID: _____	FS (field sample) FD (field duplicate) For FD, Parent ID: _____	FS (field sample) FD (field duplicate) For FD, Parent ID: _____
Field Comments:			
Entered by (Provide initials):		**Validated by (Provide initials):**	

For Data Entry Completion (Provide Initials)	Completed by	QC by

ATTACHMENT B

DUFF PREPARATION SAMPLE DATA SHEET (PSDS)

LIBBY DUFF PREPARATION SAMPLE DATA SHEET (PSDS)

Laboratory Name: _____ Lab Job No.: _____ Lab QC Batch No.: _____ SOP: DUFF-LIBBY-QU3 (Rev 0)

Preparation by: _____ Preparation Date: _____

Drying Oven Temp. (°C): _____ Muffle Furnace Temp. (°C): _____ HCL Reagent Tracking No: _____

	SAMPLE INFORMATION			DRYING					ASHING				FILTER PREP			
	Index ID	Lab Sample ID	Mass (g), as received	Tray ID(s) used in drying	Tray weight (g)	Mass (g), during drying [tray + sample] Check 1	Check 2	Check 3	Mass (g), after drying [sample only]	Pan ID(s) used in ashing	Pan weight (g)	Mass (g), after ashing [pan + sample]	Mass (g), after ashing [sample only]	Mass of ash (g) taken for analysis	Volume of HCl added (mL)	Aliquot volume (mL)	Notes
Example	X-12345	026589	500.3	A	5.71	63.12	55.90	55.84	50.13	A	15.87	36.98	21.11	0.26	15.7	1.0	
				B	4.99	70.56	63.02	63.11	58.12	B	16.20	44.05	27.85				
				C	5.23	89.63	71.85	72.03	66.8								

Note: All mass measurements should be recorded to an accuracy of ± 0.01 g.

QA Check by: Date: